Nanocrystal Synthesis and Thin Film Formation for Earth Abundant Photovoltaics

Nathaniel J. Carter
Major Professor: Rakesh Agrawal

School of Chemical Engineering
Purdue University

Providing access to on-demand energy at the global scale is a grand challenge of our time. The fabrication of solar cells from nanocrystal inks comprising earth abundant elements represents a scalable and sustainable photovoltaic technology with the potential to meet the global demand for electricity. Additionally, solar cells with $Cu_2ZnSn(S,Se)_4$ (CZTSSe) absorber layers are of particular interest due to the high absorption coefficient of CZTSSe, its band gap in the ideal range for efficient photovoltaic power conversion, and the relative abundance of its constituent elements. Our group has developed a CZTSSe device fabrication process which utilizes Cu_2ZnSnS_4 (CZTS) nanocrystal inks and yields devices with total-area power conversion efficiencies (p.c.e.) as high as 9.3%. However, the efficiencies of CZTSSe solar cells reported in literature – regardless of the device fabrication method employed – fail to exceed 12.6% due to relatively low voltages produced at open-circuit conditions (V_{OC}) under illumination.

This presentation addresses the low V_{OC} problem through the lens of challenges facing the formation of CZTSSe absorbers capable of producing high p.c.e.'s. In particular, such limitations arise from stable impurity and alloy phases as well as defect complexes involving the constituent CZTSSe elements. CZTS nanocrystals synthesized in solution are found to comprise a distribution of particle sizes and compositions. Real-time energy-dispersive x-ray diffraction studies elucidate the role of these interparticle heterogeneities in the pathway by which a CZTS nanocrystal film converts into a dense, large-grain CZTSSe absorber layer upon annealing in the presence of Se vapor. Moreover, varying the nature of interparticle heterogeneities in the nanocrystal film directly influences the V_{OC} in completed devices.

In order to probe the fundamental phenomena inhibiting the V_{OC} in CZTSSe solar cells, CZTSSe absorber films and devices are characterized in detail using various methods. Chemical-mechanical polishing of CZTSSe absorbers affords depth-profile Raman microscopy studies, indicating an increase in the S/Se ratio from the front CZTSSe surface toward the Mo back contact. Upon advanced electrical characterization via temperature-dependent current-voltage and voltage-dependent external quantum efficiency techniques, CZTSSe solar cells exhibit highly non-ideal behavior, deviating from simplified models derived from first principles that are typically applied to interpret the data from these measurements. However, modifying the models to capture the experimentally measured characteristics enables the inference of the nature of V_{OC} limitations in CZTSSe devices. Namely, nano- and micron-scale fluctuations in the CZTSSe energy band edges – arising from stable crystal defects (e.g. Cu and Zn intermixing on lattice sites) and spatial alloy composition (e.g. S/Se) variations, respectively – lead to increased recombination of photogenerated carriers and, thus, limit the V_{OC}. Future efforts are suggested to reduce the prevalence of such deleterious defects in CZTSSe absorbers, as well as to pursue alternative absorber materials that may avoid similar limitations but also comprise earth-abundant elements.